Surface Tensions of Molten Binary $CaCl_2$-NaCl, $LaCl_3$-NaCl, and $LaCl_3$-$CaCl_2$ and Ternary $LaCl_3$-$CaCl_2$-NaCl Systems

K. Igarashi, Y. Iwadate, and J. Mochinaga

Department of Synthetic Chemistry, Faculty of Engineering, Chiba University, Chiba-shi, Chiba 260, Japan

Z. Naturforsch. **42a,** 853–857 (1987); received April 23, 1987

The surface tensions of the molten binaries $CaCl_2$-NaCl, $LaCl_3$-NaCl, and $LaCl_3$-$CaCl_2$ and the three quasi-binaries $LaCl_3$-nNaCl.m$CaCl_2$ (mole ratios $n:m = 2.7:1$, $1:1$, and $1:3.1$) were measured by the maximum bubble pressure method. The surface tension of $CaCl_2$-NaCl and $LaCl_3$-$CaCl_2$ increases curvilinearly with increasing $CaCl_2$ concentration, while below 900 °C the isotherms of $LaCl_3$-NaCl show a minimum at ca. 30 mol% $LaCl_3$. A minimum was also observed for the quasi-binary with $n:m = 2.7:1$. The surface tensions for the ternary $LaCl_3$-$CaCl_2$-NaCl at 900 °C were constructed from the above results.

Introduction

Molten binary and ternary mixtures of $LaCl_3$, $CaCl_2$, and NaCl are interesting because the cations La^{3+} (1.045 Å), Ca^{2+} (1.00 Å), and Na^+ (1.02 Å) have different charge but nearly equal ionic radii [1]. In a previous study on molten $CaCl_2$-NaCl, $LaCl_3$-NaCl, $LaCl_3$-$CaCl_2$ and $LaCl_3$-$CaCl_2$-NaCl [2] it was found that the molar volumes of molten $LaCl_3$-NaCl and $LaCl_3$-$CaCl_2$ show positive and negative deviations from additivity, respectively, while those of $CaCl_2$-NaCl and the quasi-binary $LaCl_3$-nNaCl.m$CaCl_2$ ($n:m$ = mole ratio) are approximately additive. It is of much interest to see if these bulk property are reflected in the surface tension.

There exist some data on the surface tension of molten $CaCl_2$-NaCl [3] but none on $LaCl_3$-NaCl, $LaCl_3$-$CaCl_2$ and the ternary mixtures. The surface tension of $LaCl_3$-KCl has been measured in [4].

In the present study the surface tensions of the molten binaries $CaCl_2$-NaCl, $LaCl_3$-NaCl, and $LaCl_3$-$CaCl_2$, and the quasi-binaries $LaCl_3$-nNaCl.m$CaCl_2$ (mole ratios $n:m = 2.7:1$, $1:1$, and $1:3.1$) were measured and discussed.

Experimental

Chemicals and Melt Preparation

$LaCl_3$ was prepared and purified in the same way as reported in [5]. Impurities in the purified $LaCl_3$ crystal were determined by emission spectroscopy, the result being almost the same as reported in [2]. The chemicals NaCl and $CaCl_2$ were of analytical reagent grade. They were dried under vacuum of 10^{-3} Torr by heating 50 °C below their melting points for 8 hours and then melted. All the chemicals were stored in ampoules after solidification. The prepared mole ratios of the mixtures were checked by chelate titration.

Method and Procedure

As in [4], the maximum bubble pressure method was applied because of the precision of this method at high temperatures. As working gas argon was used, which was purified by passing through chemical traps filled with molecular sieves (4A) and titanium sponges at 900 °C to remove possible H_2O, N_2, and O_2. The manometer filled with di-n-butyl phthalate containing a red color dyestuff was kept at 30.4 ± 0.1 °C by thermostated water. After filling the sample cell with the working gas, its temperature was raised above the liquidus temperature as taken from a phase diagram [6, 7] and maintained within ± 1 °C with a temperature controlling device. The temperature of the melt was measured with a C.A. thermocouple sheathed with a fused silica tube.

A Pt-10% Rh alloy capillary was used for the creation of the bubble. The inside diameter of the capillary tip was determined by a measurement of the surface tension of distilled water at room temperature. For the elevated temperatures the diameter

Reprint requests to Prof. J. Mochinaga, Department of Synthetic Chemistry, Faculty of Engineering, Chiba University, Chiba-shi, Chiba 260, Japan.

0932-0784 / 87 / 0800-0853 $ 01.30/0. – Please order a reprint rather than making your own copy.

was corrected with the coefficient of thermal expansion of the alloy [8]. Details of the method are described in [4].

The surface tension, γ, was calculated by the equation

$$\gamma = r\, g\, (h\, d_1 - i\, d_2)/2 - d_2\, r^2\, g/3 - d_2^2\, r^3\, g/[12\, (h\, d_1 - i\, d_2)]\,, \tag{1}$$

where $2r$ is the inside diameter of the capillary, g the acceleration of gravity, h the height of manometer column, d_1 the density of di-n-butyl phthalate, d_2 the density of the melt, which was obtained from the molar volume data [2], i the depth of the immersion of the capillary into the melt.

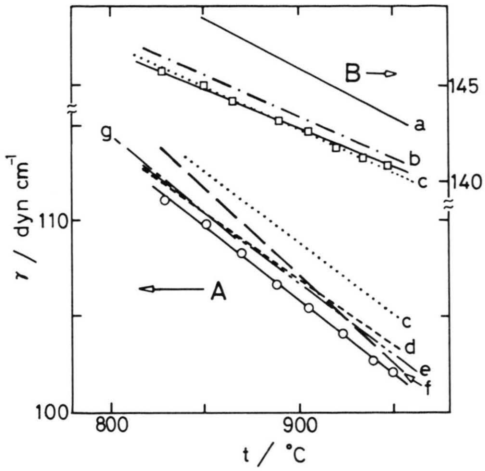

Fig. 1. Comparison of surface tensions reported in the literature with those obtained in this work. [A] NaCl (-○-), [B] $CaCl_2$ (-□-). a [9], b [10], c [11], d [12], e [13], f [14], g [15].

Results and Discussion

Pure Melts

As in [5], the surface tension of molten $LaCl_3$ could be expressed as

$$\gamma = 147.90 - 0.0423\, t\,, \quad t/°C\,.$$

Figure 1 shows the surface tensions reported in the literature with those obtained in this work for molten NaCl and $CaCl_2$. The values for molten $CaCl_2$ and NaCl recommended by Janz et al. [3, 13] are based on [11]. Our results yield smaller values, but the departures are within 1%.

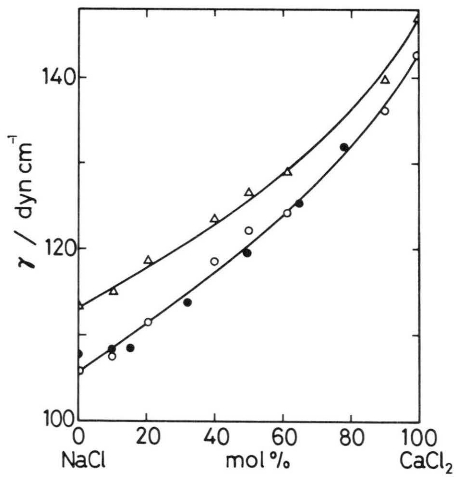

Fig. 2. Surface tension isotherms of molten $CaCl_2$-NaCl at 800 (△) and 900 (○) °C. – Symbol ● denotes the data of Grjotheim et al. [11].

Binary Melts

The surface tensions of the binary mixtures were expressed as linear functions of temperature by means of a least squares regression. The results listed in Table 1, in which δ is the standard error of estimate in dyn cm^{-1}.

Two surface tension isotherms of molten $CaCl_2$-NaCl are shown in Fig. 2 together with that reported by Grjotheim et al. [11]. The agreement with [11] is excellent. The surface tensions of this system increased curvilinearly with the increase of $CaCl_2$ concentration in both temperatures. The tendency is in good agreement with the reported one. Similar tendency was also found in a composition dependence of surface tension for the molten $LaCl_3$-$CaCl_2$ system as shown in Figure 4. On the other hand, as can be seen in Fig. 3, the isotherms of the molten $LaCl_3$-NaCl system differ evidently from those of the former two systems. That is, the isotherms at temperature below 900 °C have a minimum at ca. 30 mol% $LaCl_3$. Such a behavior is similar to that found in the composition dependence of surface tension for the molten $LaCl_3$-KCl system [5].

Recently, it has been found by Raman spectroscopy [16] that $LaCl_6^{3-}$ exists in NaCl-rich $LaCl_3$-NaCl and in $LaCl_3$-KCl [17, 18] but little of that

Table 1. Surface tensions of the molten binaries $CaCl_2$-NaCl, $LaCl_3$-NaCl and $LaCl_3$-$CaCl_2$. δ is the standard error of estimate.

$\gamma = a - b\,t$		γ/dyn cm^{-1}, t/°C		
mol%	a	$b \times 10^{-2}$	δ/dyn cm^{-1}	Temp. range/°C
(a) $CaCl_2$-NaCl ($CaCl_2$ mol%)				
0.0	173.08	7.47	0.18	830 – 950
10.0	175.48	7.56	0.06	838 – 950
20.6	174.59	6.99	0.21	830 – 940
40.1	163.06	4.93	0.26	809 – 926
50.0	164.66	4.73	0.19	824 – 945
61.4	166.40	4.69	0.32	794 – 930
90.0	179.96	4.54	0.39	811 – 950
100.0	180.84	4.23	0.23	823 – 946
(b) $LaCl_3$-NaCl ($LaCl_3$ mol%)				
10.0	160.04	5.97	0.13	815 – 933
35.1	145.37	4.39	0.21	820 – 936
50.0	149.92	4.84	0.13	853 – 940
74.8	152.53	4.84	0.05	840 – 891
90.0	148.90	4.39	0.13	874 – 945
(c) $LaCl_3$-$CaCl_2$ ($LaCl_3$ mol%)				
17.0	177.32	5.02	0.08	885 – 940
32.9	178.78	5.88	0.12	855 – 939
50.1	171.16	5.65	0.20	874 – 938
67.1	160.95	5.26	0.12	886 – 940
83.0	155.23	4.91	0.11	908 – 950

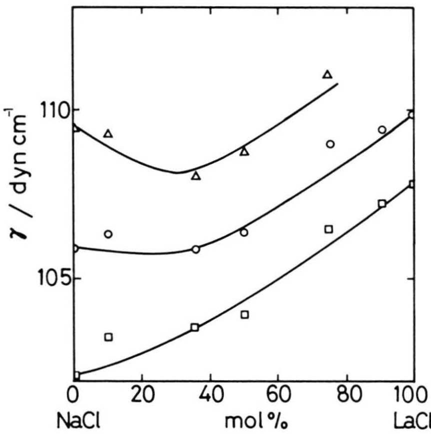

Fig. 3. Surface tension isotherms of molten $LaCl_3$-NaCl at 850 (△), 900 (○), and 950 (□) °C.

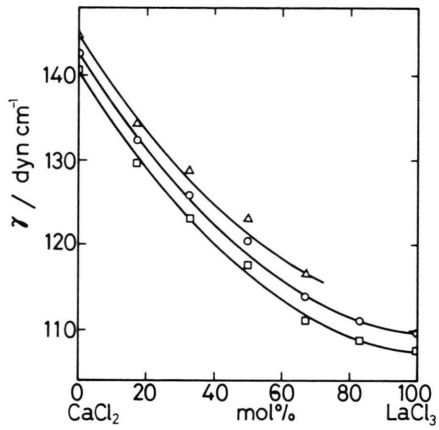

Fig. 4. Surface tension isotherms of molten $LaCl_3$-$CaCl_2$ at 850 (△), 900 (○), and 950 (□) °C.

species in $LaCl_3$-$CaCl_2$. The structure of molten $CaCl_2$-NaCl has been investigated by X-ray diffraction [19]: a calcium ion in the melt is claimed to be surrounded by about six chloride ions; the existence of this octahedral complex is however not yet confirmed. Therefore, the surface tension of molten $LaCl_3$-NaCl seems to be affected by the $LaCl_6^{3-}$ octahedron formed in the NaCl-rich melt. This is analogous to the behavior found in the surface tension of molten $MgCl_2$-KCl [11, 20], in which the existence of tetrahedral species $MgCl_4^{2-}$ has been confirmed by Raman spectroscopy [21, 22].

The surface energy of mixing per unit area, $\Delta E^s/a$, is given by [14]

$$\Delta E^s/a = E^s/a - [X_1 (E^s/a)_1) + X_2 (E^s/a)_2] ,$$

where X_1 and X_2 are the mole fractions of the components 1 and 2, respectively, and E^s/a and $(E^s/a)_i$ $(i = 1, 2)$ are the surface energies per unit area of the mixture and the constituent pure melts, respectively. They are related to the surface tension by the equations

$$E^s/a = \gamma - T\,(\mathrm{d}\gamma/\mathrm{d}T) ,$$

$$E_i^s/a = \gamma_i - T\,(\mathrm{d}\gamma_i/\mathrm{d}T) ,$$

where T is the absolute temperature. The surface energy of mixing of a molten mixture is one of the useful surface properties [20]. The calculated results for the binary systems are given in Fig. 5 together with the composition dependence of the excess molar volumes obtained in [2]. Evidently, these show an opposite composition dependence. $\Delta E^s/a$ of $LaCl_3$-NaCl, with its positive excess molar volume, its maximum being at 30 mole% $LaCl_3$, has a large negative value at the same concentration. This is similar to $\Delta E^s/a$ of $LaCl_3$-KCl [5], denoted by the dashed line. Small negative values are

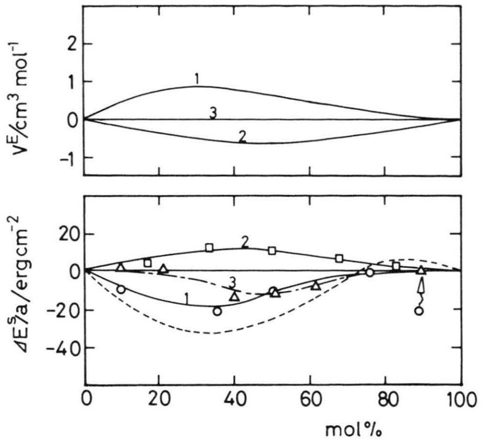

Fig. 5. Composition dependence of surface energies of mixing per unit area and excess molar volumes at 900 °C. – 1: LaCl3-NaCl, 2: $LaCl_3$-$CaCl_2$, and 3: $CaCl_2$-NaCl. $\Delta E^s/a$ of molten $LaCl_3$-KCl [4] is also shown (dashed line).

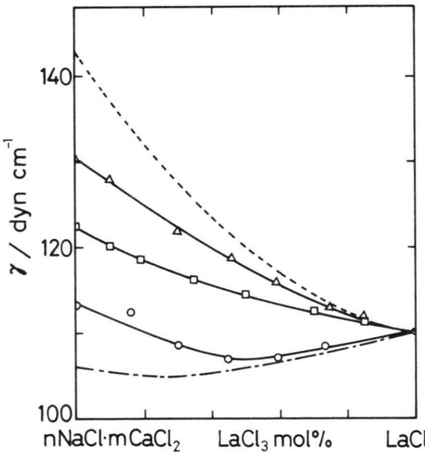

Fig. 6. Surface tension isotherms of molten quasi-binary systems at 900 °C. – (–·–) $LaCl_3$-NaCl, (○) $LaCl_3$-nNaCl.$m$$CaCl_2$ ($n:m = 2.7:1$), (□) $LaCl_3$-nNaCl.$m$$CaCl_2$ (1:1), (△) $LaCl_3$-nNaCl.$m$$CaCl_2$ (1:3.1), and (----) $LaCl_3$-$CaCl_2$.

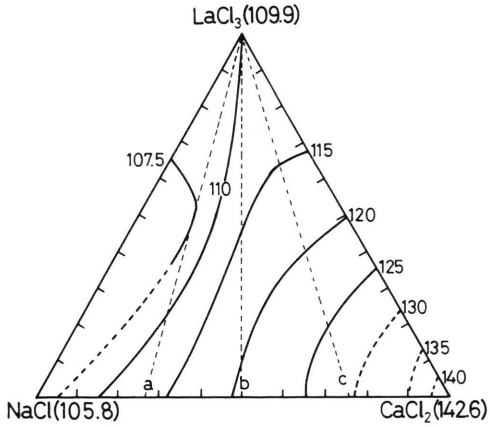

Fig. 7. Surface tension isotherms of the molten ternary $LaCl_3$-$CaCl_2$-NaCl system at 900 °C (unit: dyn cm^{-1}). – Dashed lines a, b, and c indicate the quasi-binary systems measured and dotted lines denote somewhat uncertaint isotherms.

Table 2. Surface tensions of molten quasi-binary systems.

$\gamma = a - b\,t$		γ/dyn cm^{-1}, t/°C		
mol%	a	$b \times 10^{-2}$		Temp. range/°C
(a) $LaCl_3$-nNaCl.$m$$CaCl_2$ ($n:m = 2.7:1$)				
16.8	169.69	6.38	0.19	865 – 970
30.4	150.19	4.55	0.30	882 – 955
45.1	145.04	4.20	0.30	903 – 981
59.5	148.13	4.47	0.19	870 – 975
73.1	145.90	4.18	0.08	873 – 920
(b) $LaCl_3$-nNaCl.$m$$CaCl_2$ ($n:m = 1:1$)				
10.3	155.62	3.92	0.30	811 – 946
18.8	154.52	4.00	0.13	823 – 954
35.0	152.01	3.99	0.37	842 – 934
50.0	148.93	3.83	0.45	838 – 937
70.8	145.82	3.69	0.19	851 – 950
85.5	141.26	3.29	0.14	868 – 962
(c) $LaCl_3$-nNaCl.$m$$CaCl_2$ ($n:m = 1:3.1$)				
10.2	176.09	5.27	0.34	879 – 950
30.2	172.02	5.58	0.14	840 – 972
46.0	161.02	4.67	0.15	838 – 960
59.7	145.47	3.27	0.21	836 – 951
74.5	143.09	3.16	0.19	850 – 972
89.3	144.74	3.62	0.24	865 – 962

observed for $CaCl_2$-NaCl, whose molar volume is additive. On the contrary, the $\Delta E^s/a$ of $LaCl_3$-$CaCl_2$ with its negative excess molar volume has small positive values over the whole composition range. These results show that the surface energy of mixing of molten salt mixtures is correlated with the characteristics of the melt and the excess molar volume.

Ternary Melts

The surface tensions of the molten ternary $LaCl_3$-$CaCl_2$-NaCl were measured for varying $LaCl_3$ content at constant mole ratio $CaCl_2$/NaCl, i.e. for the three quasi-binary systems $LaCl_3$-

nNaCl.$m$$CaCl_2$ with $n:m = 2.7:1$ (a), $n:m = 1:1$ (b) and $n:m = 1:3.1$ (c). The surface tensions obtained were also represented as linear functions of temperature. The parameters determined by the least squares fit are listed in Table 2. Figure 6 shows the composition dependence of the surface tension of these mixtures at 900 °C. In the $LaCl_3$-nNaCl.$m$$CaCl_2$ (2.7 : 1) system with the low concentration of $CaCl_2$, the isotherm has a minimum similar to that of the binary $LaCl_3$-NaCl. But this tendency disappears with increase of the concentration of $CaCl_2$. This appears to be due to an inhibition of the formation of $LaCl_6^{3-}$ by the presence of $CaCl_2$.

Figure 7 shows roughly the isotherms of surface tension of the $LaCl_3$-$CaCl_2$-NaCl at 900 °C according to the isotherms of the three binaries and the three quasi-binaries. The dashed lines a, b, and c indicate the quasi-binary systems measured.

[1] R. D. Shannon, Acta Cryst. **A32,** 751 (1976).

[2] K. Igarashi, Y. Iwadate, H. Ohno, and J. Mochinaga, Z. Naturforsch. **40 a,** 520 (1985).

[3] G. J. Janz, R. P. T. Tomkins, C. B. Allen, J. R. Downey, Jr., G. L. Gardner, U. Krebs, and S. K. Singer, J. Phys. Chem. Ref. data **4,** 971 (1975).

[4] K. Igarashi and J. Mochinaga, Z. Naturforsch. a, in press (1987).

[5] K. Igarashi, Y. Iwadate, J. Mochinaga, and K. Kawamura, Z. Naturforsch. **39 a,** 754 (1984).

[6] I. S. Morozov, Z. N. Shevtsosva, and L. V. Klyukina, Zhur. Neorg. Khim. **2,** 1640 (1957).

[7] K. Igarashi, H. Ohotani, and J. Mochinaga, to be submitted for publication to Z. Naturforsch. a.

[8] B. Barter and A. S. Darling, Platinum Metals Rev. **4,** 138 (1960).

[9] G. J. Janz, Molten Salts Handbook, Academic Press, New York-London 1967, p. 83.

[10] S. P. Zozyanov and V. A. Ll'icher, Russ. J. Inorg. Chem. **11,** 9 (1966).

[11] K. Grjotheim, J. L. Holm, B. Lillebuen, and H. A. Øye, Acta Chem. Scand. **26,** 2050 (1972).

[12] M. V. Smirnov, V. A. Khokhlov, and V. P. Stepanov, Electrochemistry of Molten Solid Electrolytes **7,** 31 (1969).

[13] G. J. Janz, Proc. 3rd. Int. Symposium on Molten Salts (Electrochem. Soc. USA), Proc. Vol. **81-9,** 52 (1981).

[14] H. Bloom, F. G. Davis, and D. W. James, Trans. Faraday Soc. **56,** 1179 (1960).

[15] M. F. Lantratov, J. Appl. Chem. USSR **34,** 1190 (1961).

[16] K. Ohno, K. Igarashi, J. Mochinaga, N. Umesaki, and N. Iwamoto, Proceeding of the 5th Symposium on Rare Earths, Tokyo, March 30–31, 1987, p. 140.

[17] V. A. Maroni, E. J. Hathaway, and G. N. Papatheodorou, J. Phys. Chem. **78,** 1134 (1974).

[18] G. N. Papatheodorou, Inorg. Nucl. Chem. Lett. **11,** 483 (1975).

[19] K. Igarashi, T. Nijima, and J. Mochinaga, Proceeding of First International Symposium on Molten Salt Chem. and Technol., Kyoto, April 20–22, 1983, p. 469.

[20] T. Ejima and E. Nakamura, J. Japan inst. Metals **39,** 680 (1975).

[21] V. A. Maroni, E. J. Hathaway, and E. J. Cairns, J. Phys. Chem. **75,** 155 (1971).

[22] M. H. Brooker, J. Chem. Phys. **63,** 3054 (1975).